Supporting Information

High-purity Pyrrole-type FeN₄ Site as Superior Oxygen Reduction Electrocatalyst

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Experimental Details

Catalysts Synthesis

In a typical synthesis, 2 ml aniline was dissolved into 200 ml 0.5 M aqueous HCl solution. Then 30 ml 0.6 M aqueous FeCl₃ solution was added drop wise. After stirring for 60 min at 4 °C, 20 ml 1.1 M aqueous (NH₄)₂S₂O₈ solution was added drop wise to inform the polymerization of aniline. And 400 mg Ketjenblack ECP-600 JD was added into the above solution. After stirring for 2 days at room temperature, the desired precursor was then collected and dried at 60 °C under vacuum condition. Then the precursor was pyrolysis at 900 °C for 1 h under NH₃ atmosphere. Finally, the obtained product was leached in 2 M H₂SO₄ at 60 °C for 12 h and washed thoroughly with deionized water and dried under vacuum at 60 °C. After that, the resulting material was obtained and denoted as HP-FeN₄. The synthesis procedure for traditional FeN₄ was similar with HP-FeN₄ except for pyrolysis under Ar atmosphere. NC catalyst can also been obtained by employing the similar procedure except for without adding FeCl₃.

Structure Characterization

X-ray powder diffraction (XRD) patterns were obtained by using a Philips X'Pert Pro Super diffractometer with Cu-K_a radiation ($\lambda = 1.54178$ Å). Fourier transform infrared (FT-IR) spectroscopy was measured on Nicolet 8700 FT-IR microscope. Elemental analyses were carried out on Elementar vario EL cube in CHN Mode. The transmission electron microscopy (TEM) images were obtained by employing a JEM-2100F field-emission electron microscope operated at an acceleration voltage of 200 kV. High resolution TEM (HRTEM), high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM), and corresponding energydispersive spectroscopy (EDS) mapping analyses were executed on a JEOL JEM-ARF200F TEM/STEM with a spherical aberration corrector. The nitrogen adsorptiondesorption isotherms and corresponding pore size distribution were measured using a Micromeritics ASAP 2000 system at 77 K. Raman spectra were recorded at ambient temperature with LABRAM-HR Confocal Laser Micro Raman Spectrometer 750 K with a laser power of 0.5 mW. X-ray photoelectron spectra (XPS) were obtained on an ESCALAB MK II X-ray photoelectron spectrometer with Mg K α as the excitation source. The binding energies achieved in the XPS spectral analysis were corrected for specimen charging by referencing C 1s to 284.5 eV. XAFS measurements at the Fe K-edge were performed in fluorescence mode at the beamline 1W1B of the Beijing Synchrotron Radiation Facility (BSRF, Beijing), China. C K-edge and N K-edge XANES spectra were measured at the beamline U19 of national synchrotron radiation laboratory (NSRL, Hefei) in the total electron yield (TEY) mode by collecting the sample drain current under a vacuum better than 10⁻⁷ Pa.

Electrochemical Measurements

The electrochemical tests were carried out on an electrochemical workstation (CHI 760E) in a three-electrode system. A glassy carbon electrode with a diameter of 5 mm, a graphite rod and an Ag/AgCl (saturated KCl solution) electrode were employed as working electrode, counter electrode and reference electrode, respectively. 5 mg catalyst powder and 50 μ l Nafion solution (Sigma Aldrich, 5wt %) were dispersed into 1 ml ethanol and water mixture solution (volume ratio: 3:1) and sonicated for at least 1 h to form a catalyst ink. The catalyst ink was then drop-casted onto the glassy carbon electrode with a loading of 0.6 mg cm⁻². For rotating disk electrode test, the polarization curves were recorded at a scan rate of 10 mV s⁻¹ in O₂-saturated 0.5 M H₂SO₄ solution. Electrochemical impedance spectroscopy measurements were performed by applying an AC voltage with 5 mV amplitude in a frequency range from 100 KHz to 100 mHz. Commercial Pt/C (20 wt% Pt) catalyst was used as the reference material for comparison. All of the potentials were calibrated to the reversible hydrogen electrode (RHE) according to Nernst equation.

For rotating ring disk electrode test, the disk electrode was scanned at a rate of 10 $mV s^{-1}$ and the ring electrode potential was set to 1.20 V vs. RHE. The electron transfer

number (n) and hydrogen peroxide yield (H_2O_2 %) and were determined by the following equations:

$$n = 4 \times \frac{I_D \times N}{I_D \times N + I_R} \tag{1}$$

$$H_2 O_2 \% = 200 \times \frac{I_R}{I_D \times N + I_R}$$
 (2)

Where I_D is the disk current, I_R is the ring current, and N = 0.4 is the current collection efficiency of the platinum ring.

PEMFCs tests

The catalyst inks were prepared by using catalyst, isopropanol, deionized water and Nafion solution (Sigma Aldrich, 5wt %) with a weight ratio of 1/90/30/11. The catalyst inks were ultrasonicated for 1 hour and then brushed on a piece of carbon paper with an effective area of 5 cm² until the loading reached 4 mg cm⁻². Commercial Pt/C was deposited on a carbon cloth with a loading of 0.2 mg_{Pt} cm⁻² as anode. The prepared cathode and anode were then pressed onto the two sides of a Nafion 211 membrane (DuPont) at 130 °C for 5 min to fabricate membrane electrode assemblies (MEA). The MEA was tested in a single cell and condition-controlled fuel cell test station (Scribner 850e, Scribner Associates). The cell temperature was maintained at 80 °C throughout the MEA tests. The flowing rates of H₂ and O₂ were both 400 ml min⁻¹ and the relative humidity is 100% during PEMFCs tests. Fuel cell polarization plots were recorded using in a voltage control mode at a total pressure of 200 kPa.

Computational Details

All first-principles calculations presented here were conducted with VASP,¹ version 5.4.4, which implement the kohn-Sham scheme of Density Functional Theory² into a commercial program. The main parameters which might affect our arguments were carefully chosen. The exchange correlation functional PBE³ was adopted, the energy cutoff was 500 eV, the reciprocal space was sampled using Monkhorst Pack

Scheme⁴ Γ -centered 3 × 3 × 1 k-points for the relaxation of geometry and 6×6×1 for static calculations to get accurate energy. The vacuum space is necessary in two dimensional systems to avoid the interactions between adjacent layers. In this cases, we adopted 10 angstroms. The energy and force convergence criteria were 10⁻⁴ eV and 0.05 eV/angstrom on every single atom during relaxation of geometry.

Considering the adsorption of small molecules on catalysts and poor performance of PBE functional in deal with van der Waals interactions, the DFT+D3 scheme development by Grimme⁵ was taken into account. Since the Fe atom belong to the transition metal element, such element has unoccupied d orbital and localized electrons. One mature way to cope with it in first-principles calculations was DFT+U scheme,⁶ we adopted such method to get more strictly describe of 3d electron of Fe atom, the effective U is 2.91 eV.⁷

About the configurations of catalysts, XAS results demonstrate that both HP-FeN₄ and FeN₄ exhibit typical FeN₄ configurations, which is similar to the characteristic of Heme. Therefore, a Heme-like structure was adopted in the calculations (**Figure S23**).

Gibbs free energy was criteria in our simulations, the method to calculated Gibbs free energy is based on G=E-TS+ \int CpdT. As for proton and electron transformation in ORR, we adopted the Computational Hydrogen Electrode (CHE) which was developed by Norskov.⁸ CHE model states that chemical potential of proton and electron could be substituted by H atom (1/2H₂) under standard condition (298 K, 1 Bar, pH = 0, 0 V). The correction of zero-point vibration energy was considered. Entropy and integral capacity of gas molecules is from NIST. Otherwise, entropy and integral capacity of intermediates during ORR process were calculated by DFT. We fixed the catalyst and made adsorbate vibrate, so we can collect the vibration frequency of different intermediates. There are two mechanism of ORR process: O₂ disassociation or one that does not involve O₂ dissociation.⁹ Since we are investigating single atom catalysis, we take non-dissociation mechanism is naturally option. Therefore, 4e⁻ process involved three main intermediates OOH^{*}, O^{*}, and OH^{*}, reduction of O₂ to water, while 2e⁻ process give the hydrogen peroxide which is not desired and try to avoid in fuel cell.

The elementary reaction of ORR in acid condition as follows:

$$\begin{array}{rcl} 0_2 + & * & \rightarrow 0_2^* \\ \\ 0_2^* + & H^+ + & e^- & \rightarrow 00H^* \\ \\ 00H^* + & H^+ + & e^- & \rightarrow 0^* + H_20 & \text{OR} & 00H^* + & H^+ + & e^- & \rightarrow H_20_2 \\ \\ 0^* + & H^+ + & e^- & \rightarrow 0H^* \\ \\ 0H^* + & H^+ + & e^- & \rightarrow H_20 & + * \end{array}$$

We evaluation the performance of catalysts in ORR by using thermodynamic onset potential, the value we calculated less deviation from the equilibrium potential 1.23 V, the catalyst has better catalysis ability (**Figure S24**). Of course, the concepts of thermodynamic overpotential could also evaluate the ability of catalysts. The thermodynamic overpotential at equilibrium electrode potential can be determinated according to

$$\eta = 1.23 - |\Delta G_{\min}/e^-|$$

The difference of electronic structures of two systems were presented by charge density difference, Fe in pyrrole-type FeN₄ structure has less electron accumulation on the top of Fe atom which means Fe has more positive valence state in such configuration than pyridine one. Which is consistent with experimental results. But it is worth noting that pyrrole nitrogen atom gain electrons was less than pyridine nitrogen, so we assuming ORR in such system that active site was not only just Fe-N₄, but also the nearest carbon atom should involve.

S1. TEM images of as-prepared hybrid catalysts



Figure S1. TEM images of as-prepared (a) HP-FeN₄, (b) FeN₄ and (c) NC materials.



S2. HRTEM image of FeN4 catalyst

Figure S2. HRTEM image of as-prepared FeN₄ material.

S3. XRD patterns of as-prepared hybrid catalysts



Figure S3. XRD patterns of as-prepared HP-FeN4, FeN4 and NC materials.

S4. HAADF-STEM images of as-prepared hybrid catalysts



Figure S4. HAADF-STEM images of as-prepared (a) FeN_4 and (b) HP- FeN_4 materials.

S5. EDS elemental mapping profiles of FeN4 material



Figure S5. EDS elemental mapping of as-prepared FeN₄ material.

S6. XANES of Fe K-edge for the as-prepared materials



Figure S6. Fe K-edge XANES spectra of the as-prepared HP-FeN₄ and FeN₄, as well as Fe foil, Hemin and Fe_2O_3 as references.

S7. The EXAFS fitting curves of FeN4 in the R space



Figure S7. First-shell fitting of Fourier transformations of EXAFS spectra for FeN₄ material. Top and bottom spectra are magnitude and imaginary part, respectively.

S8. The EXAFS fitting curves of FeN4 in the k space



Figure S8. Comparison between the best simulation and experimental data of Fe Kedge EXAFS oscillation of FeN₄ product.

S9. The EXAFS fitting curves of HP-FeN4 in the k space



Figure S9. Comparison between the best simulation and experimental data of Fe Kedge EXAFS oscillation of HP-FeN₄ product.

S10. BET characterization of as-prepared hybrid catalysts



Figure S10. N_2 absorption-desorption isotherm curves of (a) HP-FeN₄, (b) FeN₄ and (c) NC materials. (d) Comparison of BET surface area of HP-FeN₄, FeN₄ and NC materials

S11. Pore size distribution of as-prepared hybrid catalysts



Figure S11. Pore size distribution of HP-FeN $_4$ and FeN $_4$ catalysts.

S12. Raman spectra of different hybrids.



Figure S12. Raman spectra of HP-FeN₄, FeN₄ and NC materials.

S13. C 1s XPS spectra of different hybrids



Figure S13. C 1s XPS spectra of (a) FeN4 and (b) HP-FeN4 catalysts.

S14. FT-IR spectra of different hybrids.



Figure S14. FT-IR spectra of HP-FeN₄ and FeN₄ materials.



Figure S15. Comparison of N 1s XPS spectra for (a) FeN_4 and (b) HP-FeN₄ with NC catalysts. (c) High-resolution N 1s XPS spectra of HP-FeN₄ precursor pyrolysed for different times in NH₃ atmosphere.

S16. Fe 2p XPS spectra of HP-FeN4 and FeN4



Figure S16. High resolution of Fe 2p XPS spectra of HP-FeN₄ and FeN₄ materials.

S17. ORR stability test of HP-FeN4



Figure S17. LSV curves of HP-FeN $_4$ catalysts before and after 10 000 CV cycles.

S18. ORR stability comparison of HP-FeN4 and FeN4



Figure S18. Chronoamperometric response of HP-FeN₄ and FeN₄ materials.

S19. Open circuit voltage of different catalyst in PEMFCs



Figure S19. Open circuit voltage of HP-FeN₄, FeN₄ and NC catalysts assembled into PEMFCs

S20. Stability performance of HP-FeN4 assembled in PEMFCs



Figure S20. Stability test of HP-FeN₄ catalysts assembled into PEMFCs

S21. The electrochemical impedance spectroscopy of different catalysts for ORR process.



Figure S21. (a) Nyquist plots of HP-FeN₄, FeN₄ and NC catalysts. The fitted curves are presented by solid lines. Inset: the equivalent circuit used for fitting the Nyquist plots. (b) Comparison of the charge transfer resistance (R_{ct}) of HP-FeN₄, FeN₄ and NC.

S22. ORR activity of HP-FeN4 annealed under NH3 for different durations.



Figure S22. Oxygen reduction curves of HP-FeN $_4$ annealed under NH $_3$ for different time.

S23. 2D superlattice structure used in DFT calculations



Figure S23. Atomic structure diagrams of (a) pyrrole-type FeN₄ and (b) pyridine-type FeN₄. The balls in grey, blue, orange and pink represent C, N, Fe and H atoms, respectively.

S24. Free energy diagram for ORR



Figure S24. Free energy diagram of oxygen reduction reaction on pyrrole-type FeN_4 and pyridine-type FeN_4 .

S25. Relaxation calculations and static calculations of FeN4 system with different dense of kpoints grid.



Figure S25. (a) Relaxation calculations and (b) static calculations of pyrrole-type FeN₄ structure system with different dense of kpoints grid.

The total energy shows robust convergence with density of grid in relaxation and static calculations. As shown in **Figure S25**, the total energy difference between $3 \times 3 \times 1$ grid and $6 \times 6 \times 1$ grid are only 65 meV and 6 meV for static calculations and relaxation of structures, indicating that $3 \times 3 \times 1$ grid is dense enough to get accurate total energy. Given the fact that the lattice of supercell model adopted in our calculations are quiet

large (17 angstrom), the Monkhorst Pack Scheme in reciprocal space sampling was $3 \times 3 \times 1$ for relaxation of geometry. After the optimization of the geometry, calculation of the Gibbs free energy needs more accurate energy of reactants and products, thus we chose $6 \times 6 \times 1$ grid to get more accurate energy of structures in single point energy static calculations.



S26. Gibbs free energy of FeN4 structure with and without Fe entropy correction.

Figure S26. Gibbs free energy of pyrrole-type and pyridine-type FeN_4 structure (a) with and (b) without Fe entropy correction.

The difference of vibration frequency between Fe with and without adsorbates has also been considered during the frequency calculations. As shown in **Figure S26**, it is turns out that change of entropy of Fe atom has limited influence on Gibbs free energy. For both pyrrole-type FeN₄ and pyridine-type FeN₄, the Gibbs free energy diagrams with and without Fe entropy correction exhibit only slight difference.

S27. O₂ adsorption energy of FeN₄ with different encutoffs.



Figure S27. O₂ adsorption energy of pyrrole-type FeN₄ with different encutoffs.

S28. Gibbs free energy diagrams with respect to different ΔG .



Figure S28. Gibbs free energy diagrams with respect to different ΔG (1.23 eV of experimental value or 1.11 eV at PBE level of theory).

The Gibbs free energy diagrams of ORR with equilibrium potential of 1.11 eV at PBE level have been calculated as shown in Figure S28. Pyrrole-type FeN₄ structure exhibits lower thermodynamic overpotential of 0.27 eV than that of pyridine-type FeN₄ of 0.59 eV, suggesting higher ORR catalytic activity for pyrrole-type FeN₄. This result is also in reasonable agreement with the results calculated from 1.23 eV (experimental free energy for water splitting).

S29. Working principle and digital photographs of PEMFC.



Figure S29. (a) Working principle of PEMFC. (b) Digital photographs of a single cell assembling progress.

Sample	Pair	Ν	R (Å)	$\sigma^2 (*10^{-3} \text{ Å}^2)$	ΔE ₀ (eV)
HP-FeN ₄	Fe-N	3.8 ± 0.4	1.99 ± 0.02	8.0 ± 1.3	5.44
FeN4	Fe-N	4.0 ± 0.4	1.99 ± 0.02	8.5 ± 1.9	5.44

Table S1. Fit results of Fe K-edge EXAFS for HP-FeN₄ and FeN₄ catalysts by the IFEFFIT code.¹⁰

Table S2. Elemental composition of the samples obtained from elemental analysis(EA) and proportion of different N species calculated from X-ray photoelectronspectroscopy (XPS).

Samples	Ν	Pyridinic N	Pyrrolic N	Pyridinic N	Pyrrolic N
	(wt%)	content (wt%)	content (wt%)	content (at%)	content (at%)
FeN4	5.0	2.71	0.29	54.2	5.9
HP-FeN4	2.8	1.17	0.62	41.7	22.1

	Active area	Catalyst		
Catalyst	current density	Loading	Electrolyte	Reference
	$(mA m^{-2})$	(mg cm ⁻²)		
HP-FeN ₄	6.89	0.6	0.5 M H ₂ SO ₄	This work
FeNC-S-MSUFCs	1.29	0.82	0.5 M H ₂ SO ₄	J. Am. Chem. Soc.
				2019 , 141, 6254.
TPI@Z8(SiO2)-650-C	6.07	0.4	0.5 M H ₂ SO ₄	Nat. Catal. 2019, 2,
				259.
FeSA-N-C	3.46	0.28	0.1M HClO ₄	Angew. Chem. Int.
				<i>Ed.</i> 2018 , 57, 1-6.
SA-Fe-N	2.86	0.6	0.5 M H ₂ SO ₄	Adv. Energy Mater.
				2018 , 1801226.
(CM+PANI)-Fe-C	1.67	0.6	0.5 M H ₂ SO ₄	Science 2017, 357,
				479–484.
Co-NC	4.42	0.8	0.5 M H ₂ SO ₄	Adv. Mater. 2018,
				30, 1706758.
	4.54	0.8	0.5 M H ₂ SO ₄	Energy Environ.
Co-N-C@F127				Sci. 2019, 12, 250-
				260.
Mn-NC	3.32	0.8	0.5 M H ₂ SO ₄	Nat. Catal. 2018, 1,
				935-945.
Zn-N-C	1.99	0.5	0.1 M HClO4	Angew. Chem. Int.
				<i>Ed.</i> 2019 , 58, 1-6.

Table S3. Performance comparison between the prepared HP-FeN₄ and other reported metal-nitrogen coordination catalysts.

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